ESR study of Ni^{III} complexes with nitrosonaphthols and dithio acids

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Mixed-ligand Ni^{III} complexes with α-nitroso-β-naphthol, β-nitroso-α-naphthol, *o*-ethylxanthate, and *N,N*-diethyldithiocarbamate as ligands have been studied by ESR in liquid and frozen solutions. The degrees of symmetry distortion for the first coordination sphere of these complexes have been determined. It is shown that the transition from planar square $Ni^{II}L_2$ complexes to more stable octahedral $Ni^{III}L_2L'$ and $Ni^{III}LL_2'$ complexes occurs *via* the radical addition mechanism. A method for trapping short-lived radicals is suggested on the basis of the complex formation scheme.

Key words: complex, structure, symmetry, oximes, free radicals, ligand, ESR spectra.

The oxidation of $Ni^{II}L_2$ complexes in aprotic solvents with an excess of ligand L results in the formation of an unstable adduct $Ni^{III}L_3$. The mechanism of this process and the oxidation state of nickel(III) are poorly studied. In the majority of cases, complexes with the $3d^7$ electron configuration are in the low-spin state with an unpaired electron mainly on the $3d_{z^2}$ orbital of a metal.

The homolytic oxidation of complexes with oxime ligands, xanthates, or dithiocarbamates of Ni^{II} in the presence of PbO_2 results in the formation of paramagnetic complexes of Ni^{III} *via* the oxidative addition mechanism: $Ni^{II}L_2 + L' \rightarrow Ni^{III}L_3$, $\mathrm{LH} \xrightarrow{-\mathrm{H}^{\bullet}} \mathrm{L}'$.

In this work, symmetric and mixed Ni^{III} complexes with O,N,S-containing ligands are studied by ESR in vitrified media in order to determine their magnetic parameters and to establish specific features of their structures.

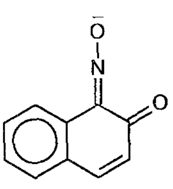
Experimental

Paramagnetic complexes $Ni^{III}L_3$ with α-nitroso-β-naphthol $Ni(OK_{\alpha\beta})_3$ (**1**), β-nitroso-α-naphthol $Ni(OK_{\beta\alpha})_3$ (**2**), *o*-ethylxanthate $Ni(T_{ks})_3$ (**3**), and *N,N*-diethyldithiocarbamate $Ni(T_{dt})_3$ (**4**) were prepared.

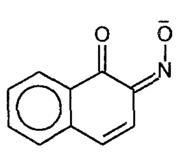
Mixed $Ni(OK_{\alpha\beta})_2T_{ks}$ (**5**), $Ni(OK_{\beta\alpha})_{20}T_{ks}$ (**6**), $Ni(OK_{\alpha\beta})_2T_{dt}$ (**7**), $Ni(OK_{\beta\alpha})_2T_{dt}$ (**8**), $Ni(OK_{\alpha\beta})(T_{ks})_2$ (**9**), $Ni(OK_{\beta\alpha})(T_{ks})_2$ (**10**), $Ni(OK_{\alpha\beta})(T_{dt})_2$ (**11**), and $Ni(OK_{\beta\alpha})(T_{dt})_2$ (**12**) were obtained by combined oxidation of complexes $Ni(OK_{\alpha\beta})_2$, $Ni(OK_{\beta\alpha})_2$, $Ni(T_{ks})_2$, and $Ni(T_{dt})_2$ in solution.

In addition, complexes with α-nitroso-β-naphthol-3,6-disulfonic acid disodium salt $Ni(OK)_3$ (**13**) and charged complexes $[Ni(KO)_2X_2]^-$, where X = Cl^- (**14**) and Br^- (**15**), were synthesized.

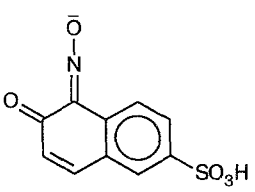
ESR spectra were recorded in toluene at 77 K on a PE-1306 spectrometer (9320 MHz), using a magnetic field calibrator mounted on a Sh-1-1 magnetic inductometer.



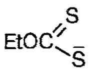
$OK_{\alpha\beta}$



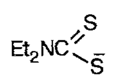
$OK_{\beta\alpha}$



OK



T_{ks}



T_{dt}

Results and Discussion

Either oximes or macrocyclic compounds with an oxime group are usually used for stabilization of NiL_3 complexes.[1] A hypothesis[1] about the ability of one oxime group to perform one-electron oxidation of nickel to form a Ni^{III} complex was advanced, and Ni^{IV} complexes were isolated[1] due to oxidation of compounds containing two oxime groups. These data were confirmed later[2,3] for Ni^{III} complexes with the tris-pyridyloxime ligand and for Ni^{IV} complexes with the bis-pyridyldioxime ligand. In all cases, the coordination of a metal in a high oxidation state to the nitrogen atom of the oxime group occurs. The deprotonated oxime group is a strong σ-donor,[2,3] which is likely caused by the high localization of a charge on the oxime nitrogen atom. Oximes usually form rather stable σ-type radicals.[4,5] The O—H bond energy in oximes is 361 kJ mol^{-1}, which is considerably greater than the similar value for hydroxyl-

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Table 1. Magnetic parameters of Ni^{III} complexes in toluene at 77 K

Complex	g_1	g_2	g_3	$\langle g\rangle$	$\Delta\langle g\rangle =$ $= \langle g\rangle - 2.0023$	ΔT	$\Delta T'$
$Ni^{III}(OK_{\alpha\beta})_3$ **(1)**	2.189	2.138	2.034	2.120	0.118	−0.024	−0.051
$Ni^{III}(OK_{\beta\alpha})_3$ **(2)**	2.195	2.142	2.034	2.123	0.121	−0.024	−0.053
$Ni^{III}(T_{ks})_3$ **(3)**	2.140	2.121	2.030	2.097	0.095	−0.009	−0.045
$Ni^{III}(T_{dt})_3$ **(4)**	2.143	2.127	2.031	2.100	0.098	−0.008	−0.047
$Ni^{III}(OK_{\alpha\beta})_2T_{ks}$ **(5)**	2.170	2.138	2.031	2.113	0.111	−0.015	−0.053
$Ni^{III}(OK_{\beta\alpha})_2T_{ks}$ **(6)**	2.172	2.139	2.031	2.114	0.112	−0.015	−0.053
$Ni^{III}(OK_{\alpha\beta})_2T_{dt}$ **(7)**	2.177	2.135	2.034	2.115	0.113	−0.020	−0.050
$Ni^{III}(OK_{\beta\alpha})_2T_{dt}$ **(8)**	2.177	2.135	2.034	2.115	0.114	−0.020	−0.050
$Ni^{III}(OK_{\alpha\beta})(T_{ks})_2$ **(9)**	2.182	2.165	2.032	2.126	0.124	−0.008	−0.066
$Ni^{III}(OK_{\beta\alpha})(T_{ks})_2$ **(10)**	2.184	2.168	2.030	2.127	0.125	−0.007	−0.068
$Ni^{III}(OK_{\alpha\beta})(T_{dt})_2$ **(11)**	2.184	2.168	2.032	2.128	0.125	−0.007	−0.067
$Ni^{III}(OK_{\beta\alpha})(T_{dt})_2$ **(12)**	2.192	2.176	2.032	2.133	0.131	−0.007	−0.071
$Ni^{III}(OK)_3$ **(13)**	2.195	2.140	2.038	2.124	0.122	−0.026	−0.050
$[Ni^{III}(OK)_2Cl_2]^{-*}$ **(14)**	2.184	2.184	2.043	2.137	0.135	0	−0.069
$[Ni^{III}(OK)_2Br_2]^{-**}$ **(15)**	2.169	2.169	2.039	2.126	0.124	0	−0.063

* HFC constant *a*(Cl) = 28 Oe, ** *a*(Br) = 14 Oe.

amines. A comparison of the deprotonated oxime group and the oxime radical shows that no change in the structure is needed on going from L′ to L^-.

It should mentioned that the CNO angle in the iminoxyl radical is larger than that in the initial oxime and is equal to the CNO angle in the coordinated oxime.[5,6] All this facilitates the oxidative addition of the iminoxyl radical to the nickel atom followed by the transfer of an electron from the nickel atom to the oxime group. To prevent solvation equilibria, uncharged complexes should be formed and aprotic solvents should be used.

The mechanism of electrochemical oxidation of $Ni(T_{ks})_2$ and $Ni(T_{dt})_2$ has been described previously.[7] Charged complexes **14** and **15** are obtained in order to compare magnetic parameters and they are also tetragonally distorted octahedrons.

The components of the *g*-tensor determined from the ESR spectra of complexes **1**—**15** are presented in Table 1. The deviation of Δg from the pure spin value g_b = 2.0023 correlates with the degree of covalency of the metal—ligand bond and with the value of deviation from the tetragonal character $\Delta T = 1 - g_1/g_2$ or $\Delta T = 1 - g_2/g_3$.

The values of Δg, ΔT, and $\Delta T'$ are close for complexes with the same ligands, for example, in the series of compounds **1**, **2**, and **13** with oxime ligands, and change on going from xanthate to carbamate ligands (see Table 1). Thus, values of magnetic parameters depend mainly on the nearest surroundings of a central ion.

The ΔT and $\Delta T'$ values characterize the structure of a complex and correlate with the degree of symmetry distortion of its first coordination sphere. Complexes **3** and **4** with three similar ligands are more symmetric, while mixed complexes with one (**9**—**12**), two (**5**—**7**), and three oxime groups (**1**, **2**, and **13**), and finally, charged complexes (**14** and **15**) are less symmetric.

The decrease in the values of *g*-factors for NiL_3 compared to NiL_2 should be mentioned. The transition from the planar square $Ni^{II}L_2$ complex to the octahedral $Ni^{III}L_3$ complex probably occurs *via* a radical addition mechanism. The octahedral complex is more stable. A similar scheme of complex formation can be used for trapping short-lived radicals.

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